LINDGREN

Determination of Nitrates in Water Analysis

Chemistry
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A Comparison of Three Methods for the Determination of Nitrates in Water Analysis

BY

JUSTA MORRIS LINDGREN

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN CHEMISTRY

COLLEGE OF SCIENCE

UNIVERSITY OF ILLINOIS

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May 31st, 1902

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Justa Morris Lindgren

ENTITLED A Comparison of Three Methods for the Determination of Nitrates in Water Analysis.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE

OF Bachelor of Arts.

Arthur W. Palmer

HEAD OF DEPARTMENT OF Chemistry.

From the remotest times the greatest value has been placed upon a supply of pure water. We find in the writings of Hypocrates and Pliny suggestions which even now-a-days may be considered well worth heeding. Not only these ancient patriarchs of science have known the dangers lurking in polluted waters, but in the last few centuries gone by the keenest apprehension has been placed upon the use of impure water, which a great many people in this last great century, have considered worthless.

The clearest crystalline water may contain the most deadly venom and on the other hand, water having a most unclean and unhealthy look may be the most healthy. One cannot tell by looking at a water what impurities it contains, it is the chemical and biological tests that do the work, therefore the importance of having absolute methods. This I think has been appreciated by

53202

the whole world. as testified by the thousands of contributions on the subject. Almost every technical journal whether chemical or not contains articles on methods and ways of obtaining pure water and of testing for impurities, and of all the methods none offer more difficulty, none are more discussed, and experimented with more, than that of determining nitrates.

Health authorities have placed the greatest importance on pure water, cities have driven artesian wells, built filter plants and in other ways spent millions of dollars in attempting to get pure water. Many states have instituted water surveys where the waters of the state may be tested free of charge, thereby collecting valuable data for health authorities and giving information of the most vital importance to the citizens.

Nitrates give the key to previous sewage contamination, but it must not be considered that water is pure when the nitrate contents are high

It indicates that the nitrogen of organic origin has been oxidized to nitrates and as such are harmless, but at the same time, it may contain other sewage contaminations together with oxidized sewage.

It indicates animal contaminations rather than vegetable, because animal matter contains more nitrogen.

Historical.

Prof. Schulze in 1861 brings out a method for the determination of nitrates which is the earliest I could find on the subject. It may be found in the Centrall Blatt No. 42. page 186 Here it is stated the nitric acid in strong alkaline solution acting upon zinc, sodium amalgam or aluminium is transformed into ammonia. This has developed later into the zinc copper couple and the zinc mercury couple methods and others.

In the July number of the Chemical News 1885 volume 52 page 42. Grandval and Lajoux give a new method for the determination

of nitrates which is now called the phenal sulphanic acid method, and which is also worked on in this thesis. It was carried on in the same way as carried on now except that the calculations of results were different and complicated.

Grandval and Lajoux were the first ones to use phenal but in the Chemical News volume 8 page 235, 1863. Phenyl was used instead of Phenal. The sample of water was evaporated down to a water bath and with a test solution of one part phenyl two parts water and three or four parts sulphuric acid where upon a reddish brown color was produced which upon making alkaline turned yellow and this yellow color compared with standards made from a solution of some nitrate of known strength. The author A. W. Hofmann L. L. D. was not ready to say whether the mono or the dinitro phenylic acid was formed, but thought this was regulated by the amount of nitrate

present.

In the Zeitschrift fur Analytische Chemie page 304 volume 2. 1869. Schulze gives a method which is now most commonly used. The reduction of nitrates in alkaline solution by means of aluminium and sodium hydroxide. To this man also together with Tiemann belongs the credit of having promulgated the Schulze-Tiemann method for the volumetric determination of nitrates by the combustion method.

F Fisher in the Journal of the Chemical Society volume 28 page 481 in 1875 introduces a method known as the indigo method.

It is this. Indigo prepared by reducing indigo by means of grape sugar, alcohol and caustic soda, oxidation in air and solution in sulphuric acid may be kept unchanged for years. Five cc of such a solution diluted with water and mixed with thirty cc of pure

sulphuric acid is titrated by running in a standard nitric acid solution, until the blue color gave place to a light green. The indigo solution is then diluted so that one c c shall be equal to .0025 milligram equivalents of nitric acid or 0.2525 milligram equivalents of potassium nitrate. If water being examined is run into four c c of the titrated indigo solution mixed with twenty c c of sulphuric acid until the blue color changes to light green. Ten divided by the number of c c of water used expresses the milligram equivalents of nitric acid per liter. If a preliminary test with brucine has shown that the water contains very little nitric acid only two c c of the indigo solution must be used or sometimes as little as one c c. If more than eight c c are required to destroy the blue color, one hundred c c must be evaporated down to eight c c and then titrated. The volume of

of sulphuric acid present must at least be double the sum of the volumes of indigo and water. The temperature must not go below 110°C

In working upon this thesis I must excuse my lack of experience in chemistry but the results I have obtained have been concientious and I think as good as could be obtained under the circumstances.

There are four important methods for the determination of nitrates. The aluminium reduction method, the Phenal-sulphonic acid method the Zinc-copper couple method and the combustion method. The last named method is conceded to be the most accurate, but because of the long time required to operate it, it is declared to be impractical for use in the water-serving laboratory.

The Aluminum Reduction Method

Boil 100 cc of the sample to be examined in a casserole to 25 cc, if the water contains free NH_3 having first added two cc of a

of a sodium carbonate solution to fix any nitric acid in solution Now transfer to a one hundred c.c test-tube adding two c.c of a solution of sodium hydroxide free from ammonia and a strip of aluminium foil. Nitrates are reduced to ammonia by the nascent hydrogen formed by the action of the sodium hydroxide solution upon the aluminium foil according to this equation

$3NaOH + Al = Al(ONa)_3 + 3H$.

Nitrites and nitrates are reduced by nascent hydrogen according to the following equations.

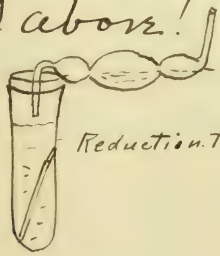
$NO_3 + 8H = NH_4OH + 3H_2O$

$NO_2 + 6H = NH_4OH + 2H_2O$

After the action has worked for twenty four hours, the contents of the reduction tube are poured into a Kjeldahl flask and diluted to about five hundred c.c. being careful to wash all the contents of the reduction tube out. Now

distill over into two-hundred cc flasks and nesslerize an aliquot part. If the nitrate contents are low distill directly into four nessler tubes and nesslerize.

In order to see if any ammonia was carried off by the escaping hydrogen. I attached a Wills bulb to the reduction tubes and allowed the hydrogen to pass through ten cc of a two and one half percent hydrochloric acid solution free from ammonia contained in the bulb. and then nesslerized the contents having first made alkaline with two cc of the sodium hydroxide solution mentioned above.



In this way I found out that a very small fraction of one percent of the contents were carried off by the hydrogen, but I did find out that some

at least was carried off.

Sodium Hydroxide Solution.

I weighed out three hundred grams of commercial sodium hydroxide and added one thousand c.c. of pure water and after cooling added about twenty five strips of aluminium foil, being about twenty centimeters long and one centimeter wide. The aluminium foil being acted upon by the sodium hydroxide formed nascent hydrogen which reduced all nitrates present to ammonia. After the action had continued until all of the aluminium was dissolved I boiled vigorously for some time until all the ammonia was driven off. I then decanted into a bottle for use.

Nesslers Solution

I dissolved sixty two and five tenths grams of potassium iodide in two hundred and fifty c.c. of water. Of this I set aside 10 c.c. I then poured in to the larger part a

Cold saturated solution of corrosive sublimate (about 7.5% solution) until the mercuric iodide precipitated was no longer redissolved upon stirring. When a permanent precipitate remained, I added the remaining ten cc of the solution so as to redissolve this precipitate. I then added corrosive sublimate until only a slight precipitate remained

Now I dissolved one hundred and fifty grams of potassium hydroxide chemically pure in about one hundred and fifty cc of pure water and added it to the above solution of mercuric iodide and potassium iodide Finally I diluted this to one liter with pure water and mixed. This has the formula of $(KI)_2 Hg I_2$ and reacts with ammonia in this way.

$NH_4OH + 2(KI)_2 HgI_2 + 3KOH = Hg_2I + 7KI + 4H_2O$

In nesslerizing place sample in a nessler tube, dilute to fifty cc if fifty cc of solution to be

nesslerized are not used. If the distillate is acid make alkaline with sodium hydroxide and then add one cc of the nessler solution as above described,

When a brownish solution is formed varying in intensity with the amount of ammonia present. This is then compared with a standard ammonium chloride solution made as follows.

Ammonium Chloride Solution

I dissolved 1.907 grams of pure resublimed ammonium chloride in one liter of pure distilled water. I then mixed this well and diluted twenty cc of this later solution to one liter with pure water. One cc of this solution contains .01 milligrams of nitrogen as ammonium chloride.

Varying amounts of this solution are taken until a color is produced upon adding nessler solution that corresponds to the color of the distillate nesslerized.

Suppose that it required six cc

of ammonium chloride, And that I used fifty cc of a two hundred cc distillate, this it would take four times as much for the entire distillate or twenty cc. But one hundred cc was the amount originally used, hence it required twenty cc of ammonium chloride for one hundred cc of the sample According to this it would require two-hundred cc for one liter which corresponds to two parts nitrogen per million since one cc of the ammonium chloride solution contains .01 grams N as NO_3.

In the chemical news volume thirty eight page one hundred and twenty one it is suggested that instead of using pure distilled water, use distilled water recently boiled with some potassium hydroxide in it. This sharpens and brightens the tests

In distilling a common block condenser was used, together with a distilling flask of eight hundred cc capacity Before distilling the

condensers were always cleaned out thoroughly, by steaming. Pummice stone was always placed in the distilling flasks to prevent bumping.

The distillation should not be too vigorous otherwise some of the contents of the distilling flask will be carried over into the receiving flask. I have had a great deal of trouble with my distillates. A great many of them were turbid or slightly so and if turbid it is almost entirely impossible to nesslerize.

I always clean my nessler tubes with a test-tube cleaner and rinced in tap-water three times and then in the best distilled water three times.

My results (see tabulated data) gave an average yield of from 85 to 90% and some times higher and lower. They were not uniform however.

The loss can be assigned to several reasons.

Perhaps all the nitrates were not reduced, part remaining behind as nitrites and as hydroxyl amine.

There must be some loss in distillation in transferring from the reduction tube to the distilling flasks, and in dripping from the condensers into the receiving flasks.

There must be some loss sometimes and sometimes some gain in making up standards. And in the accuracy of the operator in comparing the standards with the nesslerized distillate.

Sometimes the color in the glass of the nesslertubes are different and of course this effects the color inside of the tube.

Tubes varying in size change the results for instance the depth of color would not be the same in a tube higher and narrower as in one short and broad.

There is also the loss of ammonia carried off by the Hydrogen.

Warrington in the Journal of the Chemical Society / volume fifty five page five hundred and fourty four estimates the loss on nesslerization

to be fix percent.

Phenolsulphonic Acid Method.

I evaporated from 10 to 100 cc of the water to be examined in a casserole having previously added .2 cc of a solution of sodium carbonate to fix any nitric acid present.

Moistened the residue thoroughly with two cc of a phenol sulphonic acid solution $C_6H_5OHSO_3H$, being careful to moisten all parts. I then added two or three cc of pure water heated gently and made alkaline with (sod) ammonium hydroxide whereupon a bright yellow color was formed if nitrates were present.

The reactions by this method are these.

$C_6H_5OH + H_2SO_4 = C_6H_4OH\,SO_3H + H_2O$

$C_6H_4OH\,SO_3H + 3HNO_3 = C_6H_2OH(NO_3)_3 + H_2SO_4 + H_2O$

$C_6H_2OH(NO_3)_3 + NH_4OH = C_6H_2ONH_4(NO_2)_3 + H_2O$

Now I treated a solution of potassium

nitrate containing .01 milligrams of nitrogen as nitrates per cc in a similar manner placed in nessler tube and compared with the color produced by the sample of water tested

Phenol Sulphonic Acid.

Sulphuric acid pure conc.	148. cc
Distilled water pure.	12. "
Pure Phenal.	24 gr.

The above substances I mixed together and allowed to stand a few days in a colored bottle so as not to admit the light as the light decomposes the reagent.

Standard Potassium Nitrate

I dissolved .7221 grams of pure potassium nitrate in one liter of distilled water. Diluted one-hundred cc of this solution to one liter ~~of~~ with distilled water. This weaker solution contains .01 milligrams of nitrogen as nitrates in each cubic centimeter.

By this Method I got better

results than by the other two. They averaged between ninety and ninety-five percent. They were not uniform however

In evaporating down care must be taken not to allow the flame to play on the residue after evaporation because the nitrates are decomposed into NO & NO_2. The casserole should be taken off while yet a little water remains in it, and allow the heat of the vessel to do the rest.

Natural water containing chlorides give results lower than the true amount. I have not experimented with water containing chlorides but Mason say page. three hundred and eighty, that if the chlorine in the water is determined and removed by Silver sulphate the results will not be affected.

In the Journal of the Chemical Society volume XII it is stated that Chlorine does not interfere if present in less than two parts per million.

The Phenol sulphonic acid should

be freshly prepared. otherwise the yellow tint desired is not obtained but instead a greenish one is produced. which of course can not be compared.

The residue from evaporation must not be allowed to get cold, otherwise the results obtained are lower than the true ones.

The great objection to this method is the use of ammonium hydroxide This of course cannot allowed in the water + survey laboratory as it effects other results.

If some other reagent could be substituted for ammonium hydroxide this would be the best method.

Some claim that Potassium hydroxide or, sodium hydroxide could be substituted. Chemical News volume sixty four, page one hundred and twenty two.

The Journal of the Chemical Society gives some information as to the effect of (of) using old Phenol sulphonic acid

This may be found in volume sixty four page one hundred and twenty two and is as follows.

$NaNO_3$ found.	Age of reagent.
0.5	Fresh
0.5	2 day old.
0.45	2 " "
0.42	13 " "
0.40	17 " "
0.40	27. " "

In Wileys Principles and Practice of Agricultural Chemistry page five hundred and fifty six - it is claimed that the pheral sulphonic acid should be prepared some time before using, but I have found by actual experience that this is not true and the above testimony corroborates this testimony. This method does not determine the nitrites.

Great care should be taken in performing this method exactly the same each time, otherwise other nitro phenols may be

formed which have a different tint, and make comparisons difficult.

That other nitrophenols are formed can be proven from the fact that permanent standards cannot be made up from manufactured di-nitro phenol. which goes to prove that the di-nitro phenol is not the only one formed by this method. Die Chemical News. Volume sixty four page one hundred and twenty two

Great care should be taken so as not to allow sputtering of the sample in evaporating and for that reason a deep casserole should be used and small amounts of the sample.

Hence the defects of this method may be stated as follows

1. Use of Ammonium Chloride
2. Interference of other nitro phenols
3. Interference of chlorides.

The Zinc Copper Couple Method.

I used a large reducer in carrying on my determination by this method

Reducer for Zinc Copper Couple Method.

This I filled with zinc made by melting, and of irregular shape thereby offering a large surface. I then poured a weak solution of copper sulphate upon the zinc and a black coating of copper oxide was deposited upon it. Care should be taken in using a solution of copper sulphate not too concentrated as the coating in this case does not adhere well

I then washed the couples very thoroughly with pure distilled water and finally with the water to be tested. Then I placed two hundred cc of this water in the reducers and allowed the reduction to work for twenty four hours. Then I filtered this directly into a nessler tube and nesslerized directly.

In this method the nitrates are reduced by the electric current set up, decomposing the water and setting hydrogen free. This nascent hydrogen reacts upon the nitrates and nitrites forming ammonia. While the oxide unites with the zinc forming zinc oxide. The copper coating had to be replaced after using several times.

I have found results by this method to be even lower than those of the other two. The superiority of this method is in the time. It requires no distillation but can be nesslerized directly if filtered.

I have found a great deal of trouble in neutralizing the water from this method, due probably to the zinc of which some most likely goes into solution on to the oxalic acid.

Wiley in his Principles and Practice of Agricultural Analysis a Couple method by Ormandy & Cohen which he claims gives better results. This couple is made from aluminium and mercury. He says that it acts more quickly and the results obtained are more accurate. By this method he claims nitrates are reduced in one hour.

Aluminium foil free from grease is used. The foil should be heated over a bunsen flame just before amalgamation. The clean very thin aluminium foil is coated with mercury by shaking with a concentrated solution of mercuric chloride. It should be prepared immediately before use.

The amalgamated foil is introduced into the sample of water to be analyzed and left until all of the aluminium is converted into oxide. This oxide prevents bumping upon distilling. The ammonia is determined by nesslerization.

Conclusions.

The phenolsulphonic acid method gave the best results. The aluminium reduction method gave next best results and the zinc copper couple the poorest.

I think the zinc copper couple could not be used as a method because of its low results.

The results from all three methods were not uniform.

I think that a great deal of work must be done yet in perfecting a short accurate method for the determination of nitrates in water analysis

Aluminium Reduction Method.

Set	No	Parts M.	Strength	% Found.	Wills Bulb.	Remarks.
1	1	8	10	80	.001	
	2	8	10	80	.001	
	3	10	10	100	—	
	4	8	10	80	—	
2	5	6	5	120	.002	Nos 5+6 were
	6	6	5	120	.002	Not distilled.
	7	4.8	5	96	—	
	8	4.8	5	96	—	
3	9	4.4	5	88		
	10	44	5	88		
	12	4.	5	80		
	13	3.2	5	64		
	14	4.	5	80		
	15	4.8	5	88		
4	16	1.2	1.75	69.4	,014	
	17	1.2	1.75	69.4	014	
	18	1.2	1.75	69.4		
	19	1.2	1.75	69.4		
5	20	5.6	6.	93.3		
	21	5.6	6	93.3		
	22	5.6	6	93.3		
	23	5.6	6	93.3		
6				~~75~~		
7	No	record	Kept	of Strength	of Sample.	

Aluminium. Reduction Method.

Set	No	Parts M	Strength	% Found	Wills	Remarks.
8	24	.6	.6	100	001	
	25	.6	.6	100	001	
	26	.6	.6	100		
	27	.6	.6	100		
9	28	.4	1.12	35	.0005	Set number 9
	29	.4	1.12	35	.0005	dis littate very
	30	.4	1.12	35		turbid
	31	.4	1.12	35		
10	32	1.08	1.4	77		
	33	1.08	1.4	77		
11	34	1.8	1.6	105		
	35	1.8	1.6	105		
12	36		1.6			
	37		1.6			
13	38		2.4			
	39		2.4			
14	40	2.4	2.6	92.3		
	41	2.4	2.6	92.3		
15	42	2.4	3.4	141		
	43	2.6	3.4	69.3		Set 15 very
16	44	3.2	3.5	91.1		Turbid
	45	3.2	3.5	91.1		
17	46	3.6	3.6	100		
	47	3.6	3.6	100		
18	48	5.4	5.4	100		
	49	6.	5.4	111.		

Aluminium Reduction Method.

Set	No	Parts M	Strength	% Found	Mills Bulb	Remarks.
19	50	4.4	3.8	86		
	51	4.4	3.8	86		
20	52	3.6	3.7	96		
	53	3.6	3.7	96		
21	54	5.0	5.94	84		
	55	5.0	5.94	8.4		
22	56	2.0	3.3	60.6		
	57	2,0	3.3	60.6		
23	58	2.8	3.5	80.		
	59	2.8	3.5	80.		
	60	2.8	3.9	71		
	61	2.8	3.9	71		
24	62	3.7	4.3	86		
'	63	4.0	4.3	93		
25	64	4.0	4.7	85		
	65	4.0	4.7	85		

Phenolsulphonic Acid Method. J.M. Lindgren

Set	No	Parts N	Strength	% Found	% Al. Meth	% Zn Cu M	Remarks
10	1	.05	1.4	—	77		Set 10 cont
	2	05	1.4	—	77		ained Nitrites
11	3	2.3	1.72	133	105		
	4	2.3	1.72	133	105		
12	5						
	6						
13	7	No Record Kept of Strength of Sample.					
	8						
14	9	3.0	3.4	88.2	92.3		
	10	3.0	3.4	88.2	92.3		
15	11	3.0	2.6	115	141		
	12	30	2.6	115	69.3		
15	13	3.35	3.5	95.7	91.1		
	14	3.35	3.5	95.7	91.1		
16	15	3.8	3.6	105	100		
	16	3.8	3.6	105	100		
17	17	5.8	5.4	107	100		
	18	5 8	5.4	107	111		
18	19	5.4	3.8	142	86		No. 19 & 20
	20	5.4	3.8	142	86		very green.
19	21				104		
	22	Too green to compare.			64		
20	23	4.5	5.94	75.7	84		
	24	45	5.94	75.7	84		

Phenol Sulphonic Acid Method. Continued.

Set	No.	Parts N	Strength	% Found	% As Met	% Zn Cu	Remarks
21	25	3.0	3.3	90.9	60.6	60	
	26	3.2	3.3	96.9	60.6	60	
22	27	3.0	3.5	85	80	57.1	
	28	3.0	3.5	85	80	71.4	
23	29	3.4	3.9	87.1	71	102	
	30	3.3	3.9	87.1	71	76.	
24	31						
	32	Too green To compare.					
25	33						
	34.						

Copper Zinc Couple Method.

Set	No	Parts M	Strength	% Found	Phenol	Al Red.	Remarks
22	1	1.98	3.3	60	90.9	60.6	
	2	1.98	3.3	60	96.9	60.6	
23	3	2.	3.5	57.1	85	80	
	4	2.5	3.5	71.4	85	80	
22	5	3.6	3.5	102	—	—	
24	6	3.0	3.9	76	87.1	71.	
25	7	36	4.3	81	86		
	8	36	4.3	81	93		
26	9	3.6	4.7	76	95		
—	10	—	—	—			

Tabulation of results from Wills Bath.

Set	No	Wills Bulb	Strength	% of 1% in Wills
1	1	001	10	.01
	2	001	16	The amt → .01
2	3	002	5	in Wills → .05
	4	002	5	Bulb varies → 05
4	5	014	1.75	.08
	6	014	1.75	08
8	7	.6	001	.6
	8	.6	.001	.6
9	9	1.12	.0005	004
	10	1.12	0005	004